

941,384

# PATENT SPECIFICATION



NO DRAWINGS

941,384

*Inventors:* JOHN EDWARD SEAGER WHITNEY, and ALAN JOHN GILLISON

*Date of filing Complete Specification:* May 9, 1960.

*Application Date:* May 9, 1959. *No. 15968/59.*

*Complete Specification Published:* Nov. 13, 1963.

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**Index at acceptance:**—Classes C3, Q5X; B2, E1A; C3, P(2C8C, 2C13A, 2C13B, 2D1A, 2K7, 2K8, 2T2A); C3, R(1C6, 1C8, 1C15, 1P1, 1P4, 1P5).

**International Classification:**—C 08 c (C 08 d, g).

## COMPLETE SPECIFICATION

### Improvements in or relating to Vulcanisable Rubber-Resin Compositions

We, CATALIN LIMITED, a British Company, of Farm Hill Road, Waltham Abbey, Essex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to vulcanisable compositions containing a vulcanisable rubber and at least one novolak type phenol-aldehyde condensation product, to the vulcanisation of such compositions and to the vulcanised products produced therefrom.

Many attempts have been made to incorporate thermosetting resins with natural rubber in order to produce vulcanisates having a satisfactory degree of hardness as well as an adequate degree of tensile strength.

Attempts have already been made to prepare compositions containing phenolic novolak resins and natural rubber and it has been found that these two classes of materials possess limited compatibility. Accordingly, only minor proportions of such resins have hitherto been successfully incorporated with rubber. It has also been found that the tensile strength, resilience and elongation deteriorate when such resins are incorporated therewith. It has also been found in numerous instances that the resulting vulcanisates show marked phase separation on flexure. Attempts have been made to improve the compatibility of the novolak resin by the use of those based upon complex phenolic materials such as cashew nut shell liquid, but the results have still been disappointing.

A high degree of compatibility between novolak resin and rubber is not necessarily always required. Those resins which possess complete compatibility with rubbers do not necessarily impart the greatest degree of improvement thereto and it now seems that for a number of purposes optimum properties

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are secured by controlling the degree of compatibility.

In the novolak series in which formaldehyde is used as the aldehyde reactant the compatibility of the novolak with the rubber increases with increasing substitution of the aromatic nucleus. Thus, the xylanol-formaldehyde novolak resins are more compatible than the cresol-formaldehyde novolaks and the latter, in turn, are more compatible than the phenol-formaldehyde novolaks. If the formaldehyde novolak resins are replaced by the corresponding resins in which the aldehyde reactant is an ethylenically unsaturated acyclic or alicyclic aldehyde having three to ten carbon atoms in the molecule the resulting cured products are found to be completely compatible with vulcanised rubbers. Whilst the resulting products have valuable properties *per se*, cured products having outstanding properties have been found to be obtained when the novolak resin used is a mixture of a phenol- or alkylphenol-formaldehyde novolak and a second novolak resin derived from one or more of the previously mentioned ethylenically unsaturated acyclic or alicyclic aldehydes.

Accordingly, the present invention provides a vulcanisable composition containing a sulphur vulcanisable rubber, a vulcanising agent therefor, a mono- or dihydric phenol- or alkylphenol- aldehyde novolak resin in which the aldehyde is an ethylenically unsaturated aldehyde containing three to ten carbon atoms in the molecule and a curing agent for the novolak resin. Preferably the vulcanisable composition also contains a mono- or dihydric phenol- or alkylphenol-formaldehyde novolak resin. It is particularly preferred to use mixtures of a monohydric alkylphenol-aldehyde novolak resin in which the aldehyde is an ethylenically unsaturated aldehyde containing three to ten carbon atoms in the molecule ar

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5 a monohydric phenol-formaldehyde novolak resin. Cured compositions containing such mixtures, especially those containing inorganic and organic fillers, have been found to have properties which render them especially useful for a variety of purposes.

10 In the production of the vulcanisable composition in accordance with the invention when two or more novolak resins are used these may first be compounded in the desired proportions and the admixture added during the compounding of the vulcanisable composition, with or without the curing agent, or the resins may be added separately during the 15 compounding of the vulcanisable composition. A novolak resin produced from a plurality of phenols, at least one ethylenically unsaturated aldehyde containing three to ten carbon atoms and formaldehyde may also be used.

20 The novolak resins used are fusible materials and a curing agent must be included in the vulcanisable composition. Any substance which acts as a source of an aldehyde under vulcanisation conditions may be used for this purpose. A very convenient material is hexamethylenetetramine.

25 In addition the compositions should contain a vulcanising agent for the rubber. Sulphur is preferably employed for this purpose, but organic sulphur compounds which liberate free sulphur under vulcanising conditions may also be employed. Preferably at least one vulcanisation accelerator is also included in the 30 compositions of the invention.

35 When inorganic or organic reinforcing fillers are also present in the compositions of the invention vulcanisates having an outstanding combination of physical properties are obtainable. Hard vulcanisates having a useful tensile strength and satisfactory elongation are readily obtained. Inorganic reinforcing fillers such as carbon black may be used for this purpose or, alternatively, a hard organic 40 resinous filler such as a butadiene-styrene copolymer containing 80—90% by weight of styrene units.

45 The use of quite small proportions of the novolak resins derived from unsaturated aldehydes having three to ten carbon atoms together with formaldehyde novolak resins results in a marked increase in the tensile strength of the resulting vulcanise together with superior retention of physical properties of flexure. The preferred proportions of the 50 said novolak resins are from 5—25% by weight, especially 10—20%, of the total weight of novolak resins added. Larger proportions of the unsaturated aldehyde-novolak resins may be present, but there is no advantage, there being little change in the properties 55 of the vulcanisates.

60 When a filler such as a high abrasion furnace black is incorporated the use of the admixed resins results in an immediate im-

70 provement in both modulus and hardness when compared with a vulcanised filled rubber which does not include the cured novolak. A similar improvement is found with the hard organic resinous fillers, such as polystyrene and styrene copolymers containing a high proportion of styrene. The use of large proportions, e.g. up to 40—50%, of the total weight of the rubber, of a hard furnace black, results in the production of valuable materials possessing considerable gloss and graded hardness up to that of ebonite.

75 The phenol- and alkylphenol-formaldehyde novolak resins may be made by the process disclosed in our application No. 10124/57 Serial No. 880776, or may be novolak resins made from the same starting materials by other processes. In any event it is preferred that a phenol containing three unsubstituted reactive positions or a mixture of phenols containing at least 15 mol % of phenols containing three unsubstituted reactive positions be employed as starting material. Novolak resins derived from bisphenols such as diphenylopropane or from dihydric phenols, such as resorcinol, may also be employed.

80 The phenol- and alkylphenol-ethylenically unsaturated aldehyde novolak resins may be made from any acyclic or alicyclic aldehyde having three to ten carbon atoms and at least one ethylenic linkage. Thus there may be used acyclic aldehydes such as acrolein, crotonaldehyde, tiglic aldehyde or citral and alicyclic aldehydes such as furfural, thiophene-aldehydes, and their  $\alpha$ -substituted homologues having an alkyl or alkylol group having one to four carbon atoms, such as  $\alpha$ -methylfurfural and  $\alpha$ -hydroxymethylfurfural. The condensation should be carried out in the presence of a catalyst, such as zinc acetate, which effects reaction between aldehyde and phenol, preferentially to polymerisation of aldehyde or condensation product through the ethylenic linkage or linkages. The production of novolak resins from the alicyclic aldehydes may be carried out as disclosed in our application No. 5196/59, Serial No. 916775.

85 The rubber, resin or resins, vulcanising agent, accelerator and filler or fillers may be compounded upon conventional apparatus such as rollers or in a mill at temperatures between room temperature and 100°C. Care should be taken not to incorporate the curing agent for the novolak resin or resins at an unduly high temperature in order to avoid premature curing. The stocks may be applied to fabrics prior to vulcanising and, when vulcanised, have excellent adhesion to the textile base. They may also be extruded or subjected to other forming operations prior to vulcanisation. Normal vulcanisation temperatures and times may be used to cure the present compositions.

90 One of the advantages of adding the novolak resins during the compounding stage to in-

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crease considerably the plasticity of the vulcanisable mixture. This enables large proportions of the reinforcing fillers to be introduced, the milling to be accomplished more speedily, and enables the production of shaped vulcanised products having a high degree of gloss.

The use of the unsaturated aldehyde novolak resins does not retard the vulcanising action of the conventionally employed accelerators upon the rubber.

A further advantage of the invention is that the rubber used may be partially or wholly a reclaimed rubber.

The following examples illustrate the nature of this invention and the manner in which it may be performed. All tests reported were carried out in accordance with British Standards Specification No. 903/1956.

EXAMPLE I

*Resin A.* A phenol-formaldehyde novolak resin was prepared by reacting one molecular

proportion of phenol with 0.75 molecular proportion of formaldehyde, in the form of a 37% by weight aqueous solution, in accordance with the method described and claimed in our co-pending Application No. 10124/57, Serial No. 880776.

*Resin B.* A xylene-furfural novolak resin was prepared as described in our co-pending Application No. 5916/59, Serial No. 916775, by reacting one molecular proportion of a xylene fraction (obtained from the distillation of coal tar and having a boiling range of 216—220°C., which fraction consists of substantially 30% of a mixture of 3,5-xylene and meta-ethyl phenol, together with 70% of other phenols consisting predominantly of other isomers of ethyl phenol and xylene) with 0.8 molecular proportion of furfural.

The two resins were melt blended in varying proportions as set forth in Table I below and then compounded with natural rubber on a mill according to the following recipe.

		Smoked Sheet	100	parts by weight
	Resins A + B		45.5	„ „ „ „
	Hexamine		4.5	„ „ „ „
45	Zinc Oxide		5.0	„ „ „ „
	Stearic Acid		1.0	„ „ „ „
	Sulphur		2.5	„ „ „ „
	Mercaptobenzthiazole		1.0	„ „ „ „

The rubber was masticated for two minutes and the stearic acid and zinc oxide added. After milling for 5 minutes on cold rollers, the rollers were heated to 90 to 100°C., and 50 the resin or mixture of resins together with the hexamine added. Milling at this temperature was allowed to proceed for 5 minutes

after which time the rollers were cooled and the sulphur and mercaptobenzthiazole added in that order and the final blending and sheeting were achieved in an additional 5 minutes. The compounds were then cured for 20 minutes at 145°C. and tested. The results are set forth in Table I.

TABLE I

Experiment No.		1	2	3	4	5	6	7
	Resin A %	100	95	87.5	82	75	50	0
	Resin B %	0	5	12.5	18	25	50	100
	Tensile Strength (p.s.i.)	1820	2100	2344	2530	2400	2300	2240
30	Elongation at Break (%)	410	450	485	510	500	520	540
	Modulus at 200% Elongation	399	267	345	322	240	368	320
	„ „ 300% „	474	892	1060	1000	902	1180	1240
	„ „ 400% „	1795	1826	1922	1920	1850	2005	1238
	Hardness, °Shore A	52	42	45	45	45	46	43

It will be apparent from an inspection of Table I that the inclusion of as little as 5% of Resin B in the resin additive led to a marked increase in the tensile strength and this rose still further until 18% of Resin B was included in the mixture of resins used. Further increases led to little change. In the case of Experiment 1 the modulus rises sharply from 300 to 400% elongation: this is indicative of incompatibility. The latter is confirmed by the Shore hardness which falls rapidly on flexing the specimen. With as little as 5% of Resin B there is a much more gradual rise in the modulus with progressive elongation and, corresponding therewith, there

is little change in the Shore hardness on flexing the test specimen. With from 12.5—50% of Resin B there is a marked increase in the elongation at break and in all cases there is a rise in the modulus with progressive elongation and little change in the Shore hardness on flexing the test specimen.

#### EXAMPLE II

The mixture of resins used in Experiment No. 3 of Example I was compounded in varying proportions with a high abrasion furnace black using the formula set forth below and the physical properties of the vulcanisates measured.

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Smoked Sheet	100	parts by weight
Resin	Varied	
High Abrasion Furnace Black	Varied	
Hexamine	Varied	
Zinc Oxide	5.0	parts by weight
Stearic Acid	1.0	„ „ „ „
Sulphur	2.5	„ „ „ „
Mercaptobenzthiazole	1.4	„ „ „ „

The results obtained are set forth in Table II.

TABLE II

Experiment No.	1	2	3	4
Resin p.b.w.	0	9.1	22.7	22.7
Hexamine p.b.w.	0	0.9	2.3	2.3
High Abrasion Furnace Black p.b.w.	50	50	50	100
Tensile Strength (p.s.i.)	3200	3300	2500	1800
Elongation at Break (%)	400	350	250	100
Modulus at 200% Elongation	1450	2050	2000	—
„ „ 300% „	2430	2900	—	—
Hardness, °Shore A	64	78	88	96

From an inspection of Table II it will be seen that there is a marked increase in modulus and Shore hardness in those speci-

mens containing both the mixture of resins and the high abrasion furnace black. The product of Experiment 4 is an ebonite-like

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material which nevertheless still has substantial tensile strength.

EXAMPLE III

5 *Resin C.* A cresol formaldehyde novolak resin was prepared by reacting one molecular proportion of cresylic acid containing 50% of meta-cresol, the remainder being ortho and para isomers in accordance with the methods described in our co-pending Application No. 10 10124/57, Serial No. 880776.

10 *Resin D.* A cresol acrolein novolak resin was prepared by the following method.

15 108 parts by weight of mixed cresols (containing 50% meta-cresol) and 56 parts by weight of acrolein were reacted together under reflux conditions in the presence of 3.7 parts of zinc acetate dissolved in 7.5 parts by weight

of water, 0.4 parts by weight of hydroquinone being introduced as a polymerisation inhibitor. Refluxing was allowed to continue for 3.5 hours by which time the free acrolein content of the system had fallen from 32.0 to 13.8%. The unreacted acrolein together with water and other volatile matter was then removed by distillation at a pressure of 3 cm. mercury absolute pressure to a temperature of 174°C., to produce a fusible novolak resin with a melting point of 75°C.

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Resins C and D were melt blended in varying proportions and compounded with natural rubber in accordance with the recipe used in Example I. The physical properties of the vulcanisates were determined and are set out in Table III.

TABLE III

Experiment No.	1	2	3	4	5
Resin C	100	90	75	50	0
Resin D	0	10	25	50	100
Tensile Strength (p.s.i.)	1863	1998	2122	2310	2368
Elongation at Break (%)	430	460	495	525	615
Modulus at 200% Elongation	545	532	375	378	226
„ „ 300% „	1290	1208	1070	1144	458
„ „ 400% „	1750	1656	1586	1660	846
Hardness, °Shore A	52	50	45	45	41

From an inspection of Table III it will be seen that Resin C has a markedly greater degree of compatibility with rubber than Resin A since the modulus rises more gradually 40 with elongation. In this case the introduction of Resin D increases the tensile strength of the specimens and also the elongation at break. Up to 50% of Resin D can be incorporated with but a small diminution in 45 the Shore hardness.

EXAMPLE IV

50 *Composition A.* 50 parts by weight of a butadiene-styrene copolymer containing a high proportion of styrene was compounded with 100 parts by weight of smoked sheet

rubber, 5 parts by weight of zinc oxide, 1 part by weight of stearic acid, 2.5 parts by weight of sulphur and 1.4 parts by weight of mercaptobenzthiazole.

55 *Composition B.* A further compound was prepared in which 10 parts by weight of the butadiene-styrene copolymer was replaced by 10 parts by weight of a mixture of 87.5% of Resin A and 12.5% of Resin B (see Example I) together with 10% of the weight of the mixture of hexamine.

60 Test specimens were moulded at 145°C for 20 minutes and their physical properties compared.

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	A	B
Tensile Strength (p.s.i.)	1510	2800
Elongation at Break (%)	410	480
Modulus at 200% Elongation	664	977
"    " 300% "	1024	1458
"    " 400% "	—	2082
Hardness, °Shore A	63	80

5 The second specimen shows an all-round improvement in properties; the presence of the resinous mixture has greatly increased the compatibility of the mixture of the rubber and the butadiene-styrene copolymer.

WHAT WE CLAIM IS:—

1. A vulcanisable composition comprising a sulphur vulcanisable rubber, a vulcanising agent therefor, a mono or dihydric phenol- or alkylphenol-aldehyde novolak resin in which the aldehyde is an ethylenically unsaturated aldehyde containing three to ten carbon atoms in the molecule and a curing agent for the novolak resin.
2. A vulcanisable composition according to claim 1 in which there is also present a mono- or dihydric phenol- or alkylphenol-formaldehyde novolak resin.
3. A vulcanisable composition according to either of claims 1 or 2 in which the alkylphenol-aldehyde novolak resin is derived from an alkyl or polyalkyl monohydric phenol having one to four carbon atoms in the alkyl group or groups.
4. A vulcanisable composition according to any of the preceding claims in which the ethylenically unsaturated aldehyde is furfural or acrolein.
5. A vulcanisable composition according to any of the preceding claims which includes a vulcanisation accelerator.
6. A vulcanisable composition according to any of the preceding claims which includes a reclaimed rubber.
7. A vulcanisable composition according to any of claims 2 to 6 in which from 5 to 25%

by weight of the total novolak resin content of the composition is said monohydric phenol- or alkylphenol- unsaturated aldehyde novolak resin and the remainder is a monohydric phenol or alkylphenol-formaldehyde novolak resin.

8. A vulcanisable composition according to claim 1 and substantially as hereinbefore described with reference to any of the examples.

9. A process for producing a vulcanised rubber which comprises heating a vulcanisable composition according to any of the preceding claims to a vulcanisation temperature for a sufficient time to effect vulcanisation thereof.

10. A vulcanised rubber whenever produced by the process according to claim 9.

11. A mixture of a mono- or dihydric phenol- or alkylphenol-aldehyde novolak resin in which the aldehyde is an ethylenically unsaturated aldehyde containing three to ten carbon atoms in the molecule and a mono- or dihydric phenol or alkylphenol-formaldehyde novolak resin.

12. A mixture according to claim 11 containing 5 to 25% by weight of the total novolak resin content of said monohydric phenol-unsaturated aldehyde novolak resin, the remainder being a monohydric phenol- or alkylphenol-formaldehyde novolak resin.

13. A mixture according to either of claims 11 or 12 containing, as an additional ingredient, a curing agent for the novolak resins.

STEVENS, LANGNER, PARRY &  
ROLLINSON,  
Chartered Patent Agents,  
Agents for the Applicants.